Remarks

The present invention is directed to the thermolysis of carbamatooganosilanes to the corresponding isocyanatoorganosilanes. The latter compounds have a myriad of very interesting uses, but have been expensive raw ingredients due to their difficulties of preparation. This is especially true of silylisocyanates such isocyanatomethyltrimethoxysilane and isocyanatomethyl(methyl)dimethoxysilane. The latter are quite more reactive than their analogs bearing an isocyanatopropyl group.

It has long been known that carbamatoorganosilanes can be thermally cleaved to the corresponding isocyanates, with alcohol being produced as a byproduct. However, carbamatoalkoxysilanes can react with the isocyanate cleavage product, and the isocyanate cleavage product can also react with the alcohol liberated in a reverse reaction which again produces the starting carbamate. The isocyanates can also react with thermolysis to produce a number of addition products, such as carbodiimides and isocyanurates.

Thus, for example, Berger, in U.S. patents 3,598,852 and 3,607,901, disclose liquid phase pyrolysis of methylcarbamatopropyltrimethoxysilane in Example 2 of both patents (the examples are identical) at 160°C at 1mm pressure. A moderate yield of about 73% of theory was obtained. However, the process must be conducted under vacuum, and both patents indicate that if the carbamate is heated too rapidly, isocyanurate formation accompanies isocyanate formation. Since isocyanurates are solid products, they rapidly accumulate in the reaction vessel and on the walls of the apparatus. Thus, the process is limited to a batch process, and requires extensive cleaning between batches. The reaction is started to take place at 75-200°C. The reaction takes more than 5 hours for 119g. of starting material.

U.S. patent 6,008,396 was filed in 1997, almost 20 years after the issuance of the *Berger* patents, and discusses the method disclosed by *Berger* at column 1, lines 20-28, describing the yield, kinetics, and purification, and generation of by-products as deficiencies of these processes.

Thus, the '396 patent discloses a reaction in the liquid phase at higher temperature, wherein the carbamate is slowly run into a very hot inert solvent, and the isocyanate collected overhead. However, as described in the instant specification, page 1, lines 21-29, this process can only be operated semicontinuously due to the increasing concentration of impurities in the inert liquid. The reaction is conducted at 200°C to 400°C. U.S. 6,008,396 also discusses vapor phase processes, but indicates that these are unsatisfactory due to the expensive process apparatus. *Kammel et al.*, the principle reference cited by the Office, discusses the liquid phase process of the 6,008,396 patent and also the neat liquid phase process of EP-1010704, and finds these to be deficient, instead teaching a vapor phase process conducted in the presence of a heterogenous catalyst. The process takes place at 400°C to 500°C.

Claims 16-31 have been rejected over *Kammel* in view of *Greene et al.* U.S. 6,084,226 under 35 U.S.C. § 103(a). Applicants respectfully traverse this rejection.

The unexpected results achieved by the subject invention are illustrated by the Examples and Comparative Example. In the Comparative Example, a relatively small amount of methylcarbamatopropyltrimethoxysilane (20ml) is healed rapidly in an oil bath at a temperature of 225°C, in the presence of a heterogenous Fe_2O_3 catalyst. Even after 60 minutes, no overhead condensate was obtained. This is very surprising in and of itself, as 225°C is stated by *Sheridan* to be a suitable temperature for thermolysis, and *Berger* disclosed temperatures of only 75°C to 200°C. These temperatures are consistent, for example, with what one skilled in the art knows about typical substrates such as carbamatopropyltrimethoxy silane, which has a boiling point at a pressure of 10 hPa (0.01 atm) of 102°C. The boiling point at one atmosphere is not reported, because the compound exhibits severe decomposition at higher temperatures. Some estimation of the actual boiling point may be made with regard to Example 2 of the subject invention, where the overhead temperature at one atmosphere rose to 218°C. The peak head temperature will be principally governed by the highest boiling component. Isocyanatopropyltrimethoxysilane has a boiling point of 210°C, while the boiling point of methanol is quite low. Thus, the assumed boiling point of carbamatopropyltrimethoxysilane is expected to be somewhere around 218°C. This corresponds favorably to the reported atmospheric boiling point of carbamatomethyltrimthoxy silane of 204°C. The propyl compound has a slightly higher

molecular weight and thus its boiling point would be expected to be marginally higher, based on accepted chemically principles.

Both the Comparative Example and Example 2 employed the same glass apparatus, which ensures that the results are not apparatus-dependent, the same amount of starting material, and the same amount of Fe_2O_3 catalyst. The internal temperature of the reaction vessel (still) in the Comparative Example is surely above the decomposition temperature of the carbamate substrate, but must be at the boiling/decomposition temperature. Moreover, heating of only 20 ml of substrate in a 225°C oil bath clearly takes only a matter of minutes. Despite this, after one full hour of operation, no product was able to be collected as an overhead, and the amount of product in the still, 0.9 weight percent, is minuscule. At the same time, 2.6% by weight of byproducts were found, some three times the amount of product. These byproducts are substantially solid materials such as the isocyanurates which *Berger* warns against forming.

Example 2 is exactly analogous, but employed microwaves instead of an oil bath.

Even assuming that the heating to reflux in Example 2 took only a matter of seconds, product was collected for only 4 minutes, not an hour as in the Comparative Example. Yet, the total yield of product was 75 times the amount formed in the Comparative Example, and the byproducts amounted to only 20% by weight relative to the product yield. By contrast, the byproducts far outweighed product in the Comparative Example, by 300%.

In the Office Action, the Office states,

> The Examiner contends however that Greene et al. teaches microwave radiation tends to heat chemical samples very quickly (column 1, lines 20-21). Though Greene et al. does not explicitly state the rate increases, the examiner interprets the statement "very quickly" as referring to an acceleration of the rate of the reaction with microwave radiation, since the reaction rate is a heat dependent variable.

The statement that the reaction rate is a heat dependent variable is technically incorrect. Reaction rate is a <u>temperature</u> - dependent variable. Applicants acknowledge that decreasing the "time-to-temperature"[1] can affect the "apparent" rate of the reaction. Thus, for example, if a compound decomposes at 160°C and it takes only 15 minutes to effect total decomposition, the time averaged "overall" or "apparent" rate can be quite low if it takes several hours to reach 160°C. However, that is not relevant in this case, since the Comparative Example was also rapidly heated.

For example, even assuming that it would have taken 40 minutes in the Comparative Example to heat only 20 ml of carbamate substance to reflux (which is clearly not the case for such a small sample in a 225° oil bath), over the then remaining 20 minutes, still <u>no</u> overhead was collected. By contrast, directly Comparable Example 2, in only 4 minutes, produced appreciable overhead. No matter what the heat input, from no matter what source, the temperature in the reaction flask cannot be above the boiling/decomposition point. Thus, even if the microwave Example 2 heated instantaneously, it still gave a total of 75 times more product and 93% less byproduct (relative to product formed) than the Comparative Example did over a considerably longer time span, and at the same temperature (which could not have been higher than the boiling point in either case).

These results are completely surprising, unexpected, and unexplainable, even when one takes into account the possibility of more rapid heating to reflux.

Greene has no application to *Kammel*, because *Kammel* is a gas phase reaction, not a liquid phase reaction.[2] Gases cannot be heated under microwave radiation, which is well known. See, e.g., *C. Oliver Kappe, et al.*, MICROWAVES IN ORGANIC AND MEDICINAL CHEMISTRY, V. 5, Wiley-VCH ©2005, page 12 (attached).

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[1]   Heating "very quickly" in the words of *Greene*.

[2]   It is also noted that the Examiner states that *Greene* discloses a number of advantages to use of microwaves. *Greene* also states that use of microwaves is not always advantageous and lists several disadvantages. Note Col. 1, lines 34-37; Col. 1, lines 44-48; Col. 2, lines 45-47; and Col. 2, lines 57-58.

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Since *Kammel* is directed exclusively to a gas phase reaction, one skilled in the art would not be motivated to combine *Greene* to *Kammel*, as one skilled in the art recognizes that microwaves cannot heat gas. Conventional thermal methods must be used instead.

For all of the above reasons, withdrawal of the reaction of claims 16-31 over *Kammel* in view of *Greene* is respectfully solicited.

Additional non-obvious differences pertain to the dependent claims. For example, Claims 20-22 require a homogenous catalyst. A homogenous catalyst is not merely a matter of choice nor is it a routine optimization. *Kammel* is a gas phase reaction conducted in the presence of a heterogeneous catalyst. A homogenous catalyst cannot be used in a gas phase process. Therefore, these claims are further non-obvious over *Kammel* in view of *Greene*.

Claim 31 requires a gas phase reactor to be located downstream of the microwave reaction chamber. There is no reference which teaches or suggests such a configuration. To be obvious, there must be some combination of references or other teachings which would suggest such a configuration. Here, there are no such teachings. A reaction cannot be premised on the absence of a teaching.

Applicants submit that the claims are now in condition for Allowance, and respectfully request a Notice to that effect. If the Examiner believes that further discussion will advance the prosecution of the Application, the Examiner is highly encouraged to telephone Applicants' attorney at the number given below.

Please charge any fees or credit any overpayments as a result of the filing of this paper to our Deposit Account No. 02-3978.

Respectfully submitted,

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